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(54) Title: METHOD FOR PREPARING A GELLABLE STARCH PRODUCT

(57) Abstract: The present invention relates to a method for preparing a starch product, wherein an aqueous starch mixture is provided and the starch mixture is heated to a high temperature. The invention further relates to a product obtainable by such a method and to the use of such product in a variety of food applications.

Title: Method for preparing a gellable starch product

The invention relates to a method for preparing a starch product, to a starch product obtainable by such process and to the use of such a starch product.

It is known in the art to prepare a starch product suitable as a
5 texturising agent by subjecting high amylose starch to specific conditions of e.g. temperature, shear, pressure and pH.

US 5,188,674 relates to a process for jet-cooking and spray drying a polymer to recover a dried substantially amorphous polymer powder that is water soluble or water dispersible. The process may involve the recovery of a
10 starch powder, preferably a high amylose starch powder. It is described that the cooking temperature should not be too high in order to avoid degradation of the polymer, in particular in case the polymer is starch. According to US 5,188,674, the cooking temperature should be less than 162 °C in case that amylose content is less than 40 %. No process is described, wherein an at least
15 partially crystallised starch product, e.g. containing spherulites, is recovered.

US 5,131,953 relates to a pregelatinised spray-dried non-granular non-crystalline, non-retrograderd starch powder containing more than 40 % amylose. The powder may be obtained as described in US 5,188,674.

However, a need remains for alternative methodologies, that may be
20 used to prepare starch products with interesting properties for a variety of purposes.

It has now been found that by subjecting a starch with less than 50 % amylose to a specific temperature program a gellable product can be obtained with interesting properties for e.g. food applications.

25 Accordingly the present invention relates to a method for preparing a starch product, wherein

- an aqueous starch mixture - typically in the form of a suspension - is provided, which starch mixture comprises water and starch, the starch containing amylose in a content of less than 50 wt. % based on the dry substance; and

- 5 - the starch mixture is heated to a temperature of at least 170 °C.

A method according to the invention offers an easy way of preparing a gellable starch product, with interesting properties such as good spreadability, a short induction time of gelation and/or a good gel stability.

- An advantage of a method according to the invention is the
10 suitability to process unmodified starch into a product that can be classified as unmodified starch, which is required or at least preferred for many food grade applications.

Figure 1 shows a photomicrograph (crossed polars) of a gelled product according to the invention, containing spherulites.

- 15 Figures 2A and 2B show a phase contrast photomicrograph of respectively a 20 % gel according to the invention (2B) and a 20 % gel of Paselli SA2™ (2A).

- Figures 3 and 4 show photomicrographs of spreadable gels of
20 gellable starch product prepared without storage at room temperature according to Example V ((high-modulus type), Figure 3), prepared with overnight stirring at room temperature according to Example VI (spherocrystalline instant-type, Figure 4)

- 25 Figure 5 shows a rubber-like non-spreadable gel is obtained after heating suspension of gellable spherocrystalline instant-type starch product at 140 °C, cooling and storage according to Example VII.

- The starch may be starch from any natural or genetically modified botanical source. Preferred starches are cereal starches, root starches and tuber starches. Very good results have been achieved with tuber starch, in particular with potato starch. Optionally the starch is modified before heating
30 the suspension, e.g. by chemical, enzymatic and/or physical modification.

Suitable examples of chemical modifications include mild degradation by acid and acetylation of starch.

The amylose content of the starch is preferably less than 45 wt. % based upon the dry weight, more preferably less than 40 %, based upon the dry 5 weight, even more preferably less than 35 wt. % based upon the dry weight.

Very good results have been obtained with a starch comprising up to 30 wt. % based upon the dry weight. Usually, the content of amylose in the starch is more than 5 wt % based upon the dry weight. Preferably the amylose content is more than 10 wt. % based upon the dry weight. More preferably the amylose 10 content is at least 15 wt. % based upon the dry weight. Very good results have been obtained with a starch comprising at least 20 wt. % amylose based upon the dry weight. The balance of the dry substance of the starch is typically formed by components usually present in starch, in particular amylopectin and optionally some lipids and/or proteins.

15 The water in the starch mixture may be any kind of water suitable for preparing a food-grade product. Although it is possible to use distilled or demineralised water, satisfactory results have been achieved with tap water. The water is optionally supplemented with one or more additives, for example one or more pH modifiers.

20 The ratio starch to water of the starch mixture at the beginning of the heating is not particularly critical. Preferably, the starch to water ratio is at least 5:95 (wt/wt), more preferably at least 10:90. For practical reasons, the starch to water ratio is typically less than 70:30, preferably less than 50:50. For obtaining a product comprising spherulites with highly satisfactory gelling 25 properties, very good results have been achieved with starch mixture having a starch to water ratio of up to 40:60, more in particular between 10:90 and 40:60.

30 The starch mixture typically has an acidic pH, at least at the beginning of the heating. The pH may be brought to a desired value by adding a strong and/or a weak acid (buffering agent). Optionally a desired pH is at

least partially effected by the starch itself, *e.g.* when a acidic starch is used or a derivatised starch is used that releases acidic groups during the heating (*e.g.* acetylated starch which releases acetyl-groups during the heating).

The pH of the aqueous starch mixture (as measured at 25 °C) is
5 preferably less than 6.5, more preferably less than 6. The pH is usually at least 2, preferably more than 4, more preferably at least 5.

The aqueous starch mixture is heated to a temperature of at least 170 °C, preferably to a temperature between 175 and 250 °C, more preferably to a temperature between 180 and 220 °C for a duration sufficient to allow a
10 substantial disruption of starch granules; preferably until substantially all starch granules are disrupted (to form gelatinised starch), more preferably unit substantially all starch molecules are dissolved to form a starch solution.

A suitable heating time can be determined routinely based upon the information disclosed herein and common general knowledge. It may for
15 example be suitably chosen in the range of 30-600 sec, preferably in the range of 60-300 sec, more preferably in the range of 100-200 sec.

Between heating and the next step, the heated aqueous starch mixture (which is preferably a solution at the end of the heating step) may be purified, *e.g.* by filtration. However, very good results have been achieved
20 without such purification (*e.g.* filtration) of the heated starch mixture between heating and the next step.

It has been found that by further processing the heated aqueous starch mixture in a specific way, different kinds of products are obtained with interesting properties. Typical examples of further process steps include
25 cooling of the starch mixture, drying the starch mixture and crystallising at least part of the starch in the starch mixture. Further, the product may be subjected to an additional heating step, in case of a dried product preferably after having been redissolved.

After the heating step, the aqueous starch mixture (preferably a
30 solution) is typically cooled, eventually preferably to a temperature of 0-100

°C, more in particular to 0-50 °C. The skilled person will be able to employ suitable cooling rates based upon the information disclosed herein and general common knowledge. Good results have for example been obtained with cooling rates in the range of 5-200 °C/min, more in particular in the range of 40-100
5 °C/min.

Crystallisation is typically effected by cooling and/or by (spray)-drying the heated starch mixture (in particular the starch solution). In a preferred process, starch spherulites (*i.e* birefringent crystals) are formed during the crystallisation.

10 Drying may be effected in any way, *e.g.* by precipitation (typically in ethanol), lyophilising or spray-drying.

It has for example been found possible to prepare a starch product with a relatively high dynamic storage modulus, typically of at least 10 000 Pa, preferably of at least 30 000 Pa for a product comprising 20 wt. % starch in
15 water as measured by oscillatory shear rheometry, by heating the starch mixture as described above and thereafter starting to dry the resultant heated starch mixture, whilst the starch in the mixture still is essentially uncrystallised (as described in K. Svegmark, A.M. Hermansson: Shear induced changes in the viscoelastic behaviour of heat treated potato starch dispersions.
20 Carbohydr. Polym., 13, (1990), 29-45). To this effect, the heated aqueous starch mixture (in particular a solution) may be dried without first cooling the product at all or to cool it to a temperature at the beginning of the drying step of at least 20 °C, preferably of at least 50 °C, more preferably of between 70 and 100 °C. For obtaining a product with a relatively high modulus, it has
25 been found advantageous to dry the (cooled) aqueous starch mixture without any substantial storage. More in particular, the storage is typically less than 30 min, preferably 0-15 min, in this embodiment.

Very good results have been achieved with a method wherein the drying is realised by spray drying. Optionally, the heated starch mixture is

diluted, e.g. to obtain a solution of 5-10 wt % starch in water, before being dried.

In a method wherein the starch is spray-dried, a product is obtained that forms a thermo-reversible gel with a relatively high modulus when 5 contacted with water. Such a high modulus product has been found very suitable for application as a fat replacer, in particular in a spread, or as a caseinate replacer, in particular in imitation cheese. Further, such a high modulus product has been found suitable as a transparent or opaque film with good moisture barrier properties (e.g. comparable to gelatin). It may for 10 example be suitably applied to a surface of a foodstuff by solution casting a composition of the starch product in water to the surface. Such a high modulus product has also been found very suitable as an expansion aid for a food stuff or as a chocolate grating. In addition, such a high modulus product may be used as a thermoreversible gelling starch product.

15 In an alternative method according to the invention, it has for example been found possible to prepare a spreadable starch product, which has been found very suitable in an application wherein instant gelling or texturising is required or desired. Such a method comprises subjecting an aqueous starch mixture, in particular a suspension, to a heating step as 20 described above and thereafter cooling the starch product before optionally drying it. The cooling is preferably carried out to a temperature of 100 °C or less, more preferably to a temperature in the range of 10-50 °C. Then the cooled starch mixture is preferably stored for at least 30 min, preferably up to 50 hours, more preferably for 12-36 hours, before optionally being dried, e.g. by 25 spray drying. During storage, at least part of the starch typically crystallises to form spherulites. The storage may be carried out without agitating the starch product. For practical reasons, in particular on a large production scale, the storage usually takes place under some motion of the starch product. A thus obtained starch product has been found to have an attractive ointment-like 30 character.

After storage, the product may be suitably dried or directly further processed, e.g. used in a foodstuff. Drying is for example carried out by precipitation of the starch in an organic liquid, such as ethanol, by lyophilisation, by roll-drying or by spray-drying. For practical reasons, spray 5 drying is preferred. Thus, a dried starch product is obtained that is instant gellable, i.e. suspendable in cold water (e.g. of about 15-30 °C) to form a gel. Such a gel has been found to have good spreading characteristics. It can for example readily be spread on a sandwich. A particular advantage of an instant gellable product in accordance with the invention is the capability to form a gel 10 in cold water, without lumps.

A spreadable starch product which is thus obtainable has been found to be very suitable in a variety of spreadable foodstuffs. For example, it may serve as a caseinate replacer in imitation cheese, as a thickening agent in e.g. sauces, spreads and the like, as a fat-substitute e.g. in low-fat ice-cream or 15 chocolate spread.

A method according to the invention may further comprise additional steps to further alter the characteristics of the starch product. For example the texture of a starch product, in particular a spreadable starch product may be smoothened, e.g. with high-speed mixer (e.g. an Ultra-Turrax), 20 or a colloid mill or homogeniser, which leads to a reduction of the dynamic shear modulus

For some purposes it is advantageous to suspend a starch product obtainable in accordance to the invention, in particular a spreadable product containing spherulites and subject the suspension to a heating step to obtain a 25 rubbery, non-spreadable gel. The temperature is preferably raised to a temperature at which starch crystals, in particular spherulites, irreversibly dissolve. The chosen temperature is typically at least 80 °C, preferably about 120-180 °C, more preferably about 130-150°C. Thus a rubbery gel-like product is obtained, which may be used as a carrageenan replacer. Such a product has

also been found to be very satisfactory in UHT foodstuffs e.g. to form a smooth cuttable pudding that is stable at room temperature.

A method according to the invention has been found to be very suitable to be carried out in a continuous way or in a partially continuous way.

- 5 In particular the heating step is preferably performed continuously, more preferably in a jet-cooker.

The present invention further relates to a starch product, obtainable by a method according to any of the preceding claims. Examples of such a product in particular include gellable starch powders, thermoreversible starch 10 gels, spreadable gels and rubber-like starch gels.

A thermoreversible gel according to the invention typically has a melting temperature below 125 °C, preferably below 100 °C.

The weight average molecular weight (M_w) of the starch molecules in the product may be in the range of 10 000 – 25.10⁶ g/mol. preferably M_w is 15 at least 50 000 g/mol, more preferably at least 100 000 g/mol. M_w is preferably less than 18.10⁶ g/mol, more preferably less than 10.10⁶ g/mol. M_w as used herein is the value as is determinable by SEC-MALLS-RI (size exclusion chromatography-multi angle laser light scattering-refractive index detection) with as an eluent DMSO/0.1 M aqueous NaNO₃ (90/10 v/v) on a PLGel Mixed- 20 D/Mixed E column at 95 °C , as described in S.H. Yoo, J.L. Jane. Molecular weights and gyration radii of amylopectins determined by high-performance size-exclusion chromatography equipped with mult-angle laserlight scattering and refractive index detectors. Carbohydr. Polym., 49, (2002), 307-314..

Of a gellable product according to the invention, it has been found 25 that it contains a relatively high amount of amylase-resistant starch. Amylase-resistant starch is defined as starch that is not digestible by pancreas amylase at 37 °C and pH 5.2, as determined by the Englyst method (3. H.N. Englyst, S.M. Kingman, J.H. Cummings. Classification and measurement of nutritionally important starch fractions. Eur. J. Clinical Nutr., 46 (Suppl.2), 30 (1992), S33-S50)

Preferably the non-degradable (*i.e.* resistant) starch content is less than 40 wt. %, based upon the dry substance, more preferably 1-40 wt. %, even more preferably between 15 and 30 wt %.

The present invention further relates to a foodstuff comprising a starch product in accordance with the invention. Examples of such foodstuffs include snacks, desserts (in particular instant desserts, low-fat desserts and cuttable puddings), imitation cheeses, chocolate and chocolate substitutes, low-fat spreads, low-fat margarine, cold-process spoonable products and sauces.

A product according to the invention is very suitable to form a film, e.g. on a food stuff, which film acts as a moisture barrier.

The present invention further relates to the use of a starch product as describes herein as a gelling agent, a texturising agent, a moisture barrier, a fat substitute or an expansion aid.

When used as a gelling agent the amount of starch product is preferably at least 3 wt %. For such purpose, the starch may for instance be used in a low-fat margarine or a cuttable pudding, *e.g.* in a concentration of about 5 wt. % based on the dry product

Very good results as a fat-replacer have been achieved in concentration of up to 20 wt %.

The invention is now further illustrated by the following examples.

Example I

A 20 wt % (dry matter basis) potato starch suspension in distilled water was prepared in a stainless steel DSC cup. After hermetically sealing 5 the cup, the suspension was heated in a DSC instrument to 190 – 210 °C at a heating rate of 10 °C/min, and thereafter quench-cooled (200 °C/min) to room temperature. After direct opening of the cup, a clear solution was obtained. After overnight storage of this solution at room temperature, a gel with a greasy texture was obtained. Microscopically, this gel consisted of birefringent 10 spherulites. Heating the gel so obtained in a hermetically sealed cup in a DSC instrument gave a melting transition between 35 and 90 °C with a peak temperature of 63 °C. This melting transition could be recovered in the same gel after overnight cooling at 4 °C. (This example demonstrates the spherocrystalline and thermoreversible nature of gels obtained from aqueous 15 starch heated to > 170 °C).

Example II

A 20 wt % (d.m. basis) potato starch suspension in demineralised 20 water was gelatinised at 100 °C, then heated in a hermetically sealed stainless steel cylinder in an air oven adjusted so as to give a temperature rise of the suspension to 185 °C at 10 °C/min, and quench-cooled in two steps to room temperature. After overnight storage of the clear solution at room temperature, a gel with spherulite texture was obtained. A gellable starch 25 product in powder form was obtained (a) by dehydrating the gel by freeze drying, or (b) by diluting the gel with some water to obtain a pourable gel suspension, which was precipitated by adding the suspension to 10 volumes of ethanol with stirring, and vacuum-drying the ethanol-washed precipitate. A 20 wt % (d.m. basis) suspension of the dried gellable starch product in 30 demineralised water was heated to 100 °C and loaded into a dynamic spectrometer thermostatted at 20 or 4 °C, in order to follow the dynamic

storage modulus G' as a function of time. After 16 h at 20 °C, G' attained 14100 Pa with zero induction time (where induction time is defined as the time required to develop a value of G' significantly different from 0). After 16 h at 4 °C, G' attained 58600 Pa with zero induction time. For a 20 wt % (d.m. basis) aqueous potato maltodextrin (Paselli SA2) gel prepared in the same way, G' values after 16 h were 2300 (20 °C) and 23000 Pa (4 °C), whereas induction times were 3.3 and 0.4 h, respectively. (This example demonstrates the preparation of a gellable starch product and its gelling ability.)

10 **Example III**

A dry gellable starch product was made according to Example II. A 20 wt % (d.m. basis) suspension of this starch products in demineralised water was prepared at room temperature and loaded into a dynamic spectrometer thermostatted at 20 or 4 °C, in order to follow the dynamic storage modulus G' as a function of time. After 16 h at 20 °C, G' attained 5500 Pa with zero induction time (where induction time is defined as the time required to develop a value of G' significantly different from 0). After 16 h at 4 °C, G' attained 22200 Pa with zero induction time. A 20 wt % (d.m. basis) Paselli SA2 gel prepared at the same conditions did not exhibit instant properties. (This example demonstrates the instant character of the gellable starch product.)

25 **Example IV**

Dry gellable starch products were made according to the general method described in Example II, based on waxy maize starch (0 % amylose), tapioca starch (17 % amylose), potato starch (21 % amylose), normal maize starch (26 % amylose), and high-amylase maize starch (63 % amylose). Final heating temperature is listed in the Table below. Suspensions of the dried gellable starch product in demineralised water were heated to 100 °C and

loaded into a dynamic spectrometer thermostatted at 20 °C, in order to follow the dynamic storage modulus G' as a function of time. The dynamic storage modulus G' after 16 h storage and the weight average molar weight Mw of the resulting gels are listed in Table I. (This example demonstrates the effect of starch type on gelling properties).

Table I

Starch	Gel concentration (wt %)	Final heating temp in making gellable starch product (°C)			
		180		190	
		G' (Pa)	Mw (x 10 ⁶)	G' (Pa)	Mw (x10 ⁶)
Waxy maize	20	0		0	
Maize	20	6500	16.5		
HA-maize	10	5100	3	21000	1.5
Tapioca	30	220	3.9		
Potato	20	14100	2.3	16800	0.68

Example V

10

A 20 wt % (d.m. basis) potato starch suspension in tap water was prepared and adjusted to pH 5.5. The suspension was jet-cooked at 180 °C for 160 s, and the hot starch solution was directly fed into a spray-drier to make a dry gellable starch product. This product had an aggregate-type morphology (see Figure 3). Suspensions of this dried gellable starch product in water 10 °DH were either heated to 100 °C and loaded into a thermostatted dynamic spectrometer, or directly loaded in to the spectrometer, in order to follow the dynamic storage modulus G' at a temperature specified in Table II. The dynamic storage moduli G' as a function of time are listed in Table II. (This example demonstrates the manufacture and the gelling properties of non-crystallised, directly spray-dried gellable high-modulus type starch product).

15

20

Table II

Starch	Conc (%)	Treatment ^b	Storage temp (°C)	G' (Pa) as function of storage time		
				0 h	2 h	16 h
GSP ^a	8	Cook-up	4	0	7	950
	10	Cook-up	4	0	976	5130
	10	Cook-up	20	0	74	3020
	15	Cook-up	20	0	10930	23340
	15	Instant	20	4	5760	12650
Paselli SA2	20	Cook-up	4	0	4110	23040
	20	Cook-up	20	0	1	2290
	20	Instant	20	0	10	1000

a: GSP = gellable starch product; b: cooking up before gelling (cook-up) or mixing gelling agent and water at room temperature (instant).

Example VI

- A 20 wt % (d.m. basis) potato starch suspension was heated as described in Example V, then cooled rapidly to room temperature by using a cooling section at the jet-cooker, and stored overnight at room temperature with continuous stirring at 24 rpm in order to crystallise part of the starch. The recrystallised starch suspension was homogenised and fed into a spray-drier to obtain a dry gellable starch product. This product has a spherocrystalline morphology. The gelling properties of this product were evaluated as described in Example V (Table III). (This example demonstrates the manufacture and the gelling properties of a spherocrystalline instant-type gellable starch product.)

Table III

Starch	Conc (%)	Treatment ^b	Storage temp (°C)	G' (Pa) as function of storage time		
				0 h	2 h	16 h
GSP ^a	20	Cook-up	20	96	305	1695
	25	Instant	4	60	1730	29990
	25	Instant	20	41	851	7240

a: GSP = gellable starch product; b: cooking up before gelling (cook-up) or mixing gelling agent and water at room temperature (instant).

Example VII

A 10 % suspension in tap water 10 °DH of a dry gellable starch
5 product prepared as described in Example VI was heated in an autoclave at
140 °C for 5 minutes. After overnight storage of the resulting solution, a
rubber-like non-spreadable gel was obtained. When the described treatment at
140 °C was performed with the dry gellable starch product prepared as
described in Example V, a spreadable particle gel was obtained after overnight
10 storage at 20 °C. (This example demonstrates the use of spherocrystalline
instant-type gellable starch product as a starting material for making rubber-
like gels).

Example VIII

15 Gellable starch products, prepared according to Examples V and VI,
were tested for their amylase-digestibility according to the Englyst method (as
in the reference cited above), both when mixed with water at ambient
temperature and after heating at 100 °C and overnight storage at 20 °C. The
20 results are shown in Table IV. (This example demonstrates the presence of
amylase-resistant and slowly digestible starch in the gellable starch products,
both in instant and in cook-up and store applications).

Table IV

GSP ^a prepara- tion method	Sample treatment	RDS ^b	SDS ^b	RS ^b	Mw ^c (g/mol)
Example V ^d	Instant	16.2	55.3	28.5	2 100 000
Example VI		51.0	24.4	24.6	1 800 000
Paselli SA2		54.3	26.4	19.3	270 000
Example V ^d	Cook / store	36.8	37.0	26.2	
Example VI		46.2	29.1	24.7	
Paselli SA2		49.9	31.5	18.6	

a: GSP = gelling starch product; b: RDS, SDS, RS are rapidly digestible starch, slowly digestible starch, and amylase-resistant starch, determined according to the method described in Reference 3; c: Mw = weight average molecular weight; d: sample difficult to disperse.

5

Example IX

The gellable high-modulus type starch product, prepared as
10 described in Example V, was applied as the sole hydrocolloid in the preparation of a 40 % fat spread (light margarine) according to the state of the art. The amount of gellable starch product in the final spread was 5.0 wt % (d.m. basis) with no other added hydrocolloids. The final spread showed good external structure, spreadability, and sticking to knife with no loose water.

15

Example X

The gellable high-modulus type starch product, prepared as described in Example V, was applied as a caseinate replacer in imitation
20 cheese. An imitation cheese was prepared according to the state of the art, containing as the major components cocoa fat (21.8 %), sodium caseinate (22 %), gellable starch product (4 %), and water (48 %), in order to achieve 15 %

caseinate replacement. The obtained imitation cheese showed good melting and shredding properties.

Example XI

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The gellable instant type starch product, prepared as described in Example VI, was applied as a fat replacer in chocolate spread. Gellable starch product (18.7 wt % (d.m. basis)) and soft sugar (10.0 %) were mixed with hot chocolate milk, the mixture was treated with a high-speed mixer, then stored 10 at 4 °C to obtain a low-fat chocolate paste with good spreading properties for use on e.g. sandwiches.

Example XII

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The gellable instant type starch product, prepared as described in Example VI, was applied as a fat replacer in vanilla ice cream. Evaporated low-fat (4 %) milk (52 parts) was diluted with water (14.6 parts). Part of the diluted liquid was added to a composition of gellable starch product (16.7 parts (d.m. basis)) and vanilla sugar (16.7 parts) with stirring. After addition of the 20 remaining liquid, the mixture was agitated to obtain an aerated structure, which was stored at -18 °C.

Example XIII

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The gellable instant type starch product, prepared as described in Example VI, was applied as a gelling agent and carrageenan replacer in a dairy dessert. An aqueous suspension of gellable starch product (5.1 wt % (d.m. basis) was heated at 140 °C for 5 min and cooled to 80 °C, whereafter soft sugar (9.4 %), low-fat milk powder (7.8 %), and dextrose monohydrate (5.5 %) 30 were added. The composition was mixed and stored at 4 °C for at least 24 h to

yield a pudding with a rubbery gel type texture, which showed good cutting properties and stability against bleeding.

5 **Example XIV (starch films)**

Films were prepared by casting a 10 % solution of gellable high-modulus starch product, prepared according to Example V (dissolved in water at 100 °C or at 120 °C) and drying the cast solution for 2 hours at 80 °C. An
10 opaque film was obtained from the starch product dissolved at 100 °C, a transparent film was obtained from the starch product dissolved at 120 °C. Both films were of food-grade and has moisture barrier properties.

15 **Example XV (barrier film on biscuit)**

A gellable high-modulus type starch product prepared according to Example V was mixed with water (10 wt % starch) and heated for 10 min. at 120 °C and cooled to 50 °C. Thereafter biscuits were coated with the cooled solution by brushing and then dried for 30 min at 90 °C.

20 Moisture barrier properties were measured by storing at 20 °C and 80 % RH. Moisture transport was measured by weighing in time. The results were compared with a blanc and with gelatin as a moisture barrier. The results are shown in the following Table V.

Table V

storage time	Absolute increase of weight (grams/biscuit)		
	Blanc	Gelatine	starch retrogel
1 day	0.44	0.12	0.12
5 days	0.56	0.42	0.38
>10 days	0.6	0.52	0.5

Example XVI (expansion improver)

5

30 wt % in water of a starch product according to Example V was heated for 10 min at 120 °C and thereafter dried at 100 °C. The resultant product was extruded at 190 °C in oil. A fine porous structure was obtained the expansion factor (thickness after extrusion/before extrusion) was 3.5.

10

Claims

1. Method for preparing a starch product, wherein
 - an aqueous starch mixture is provided, the starch containing amylose in a content of less than 50 wt. % based on the dry substance; and
 - the starch mixture is heated to a temperature of at least 170 °C.
2. Method according to claim 1, wherein the starch mixture is heated to a temperature between 175 and 250 °C, preferably between 180 and 220 °C.
3. Method according to claim 1 or 2 wherein, after the starch mixture has been heated, at least a substantial part of the starch is crystallised during a crystallisation step.
4. Method according to claim 3, wherein during the crystallisation step starch spherulites are formed.
5. Method according to claim 3 or 4, wherein the heated starch mixture is cooled to a temperature in the range of 0-100 °C, preferably 0-50 °C, before, during or after the crystallisation.
6. Method according to any of the preceding claims, wherein the starch mixture is dried after being heated.
7. Method according to claim 6, wherein the starch mixture is dried by spray drying.
8. Method according to claim 6 or 7, wherein the temperature of the starch mixture at the start of the drying is at least 170 °C, preferably 180-220 °C.
9. Method according to claim 6 or 7, wherein the starch mixture is dried after being cooled to a temperature below 170 °C, preferably after being cooled to a temperature of 100 °C or less.

10. Method according to claim 9, wherein the heated starch mixture is cooled to a temperature in the range of 10-40 °C, then stored for at least 30 min. – optionally under motion – and thereafter dried.
11. Method according to any of the claims 6-9, wherein the starch 5 remains essentially uncrosslinked until the drying is started.
12. Method according to claim 11, wherein the heated starch mixture is cooled to a set-point temperature between 20 and 220 °C, preferably between 70 and 100 °C, and essentially immediately upon reaching the set-point temperature the starch mixture is dried.
- 10 13. Method according to any of the preceding claims, wherein at least part of the process is carried out in a continuous way.
14. Method according to claim 13, wherein heating is carried out by continuous cooking, preferably in a jet cooker.
15. Method according to any of the preceding claims, wherein the pH of the starch mixture before heating (as measured at 25 °C) is between 2 and 7, 15 preferably between 4 and 6.5, more preferably between 5 and 6.
16. Method according to any of the preceding claims, wherein the water is tap water, optionally supplemented with one or more additives.
17. Method according to any of the preceding claims, wherein the starch 20 is cereal, root or tuber starch, preferably potato starch.
18. Method according to any of the preceding claims, wherein the starch is a chemically, enzymatically or physically modified starch.
19. Method according to any of the preceding claims, wherein the amylose content of the starch is between 5 and 45 wt. % based upon the dry 25 substance, preferably between 10 and 40 wt. % based upon the dry substance, more preferably 15-30 wt % based upon the dry substance.
20. Starch product, obtainable by a method according to any of the preceding claims.
21. Starch product according to claim 20, wherein the starch product is 30 a gellable starch powder, a spreadable gel or a rubber-like gel.

22. Starch product in the form of a spreadable thermoreversible gel, comprising starch spherulites.
23. Starch product according to any of the claims 20-22, which is gellable in water at 20 °C.
- 5 24. Starch product according to any of the claims 20-23, wherein the starch has a weight average molecular weight as determinable by SEC-MALLS-RI in the range of 10 000 – 25.10⁶ g/mol, preferably 50 000 – 20.10⁶ g/mol, more preferably 1.10⁵ – 10.10⁶ g/mol.
- 10 25. Foodstuff, comprising a starch product according to any of the claims 20-24.
26. Film, at least consisting of a starch product according to any of the claims 20-24.
- 15 27. Use of a starch product according to any of the claims 20-24 as a gelling agent, a texturising agent, a moisture barrier, a fat substitute or an expansion aid.

Figure 1:

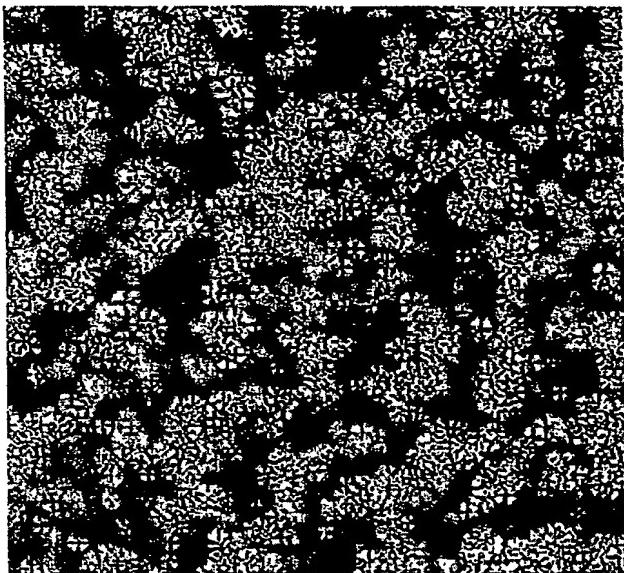


Figure 2A (Paselli SA2™)

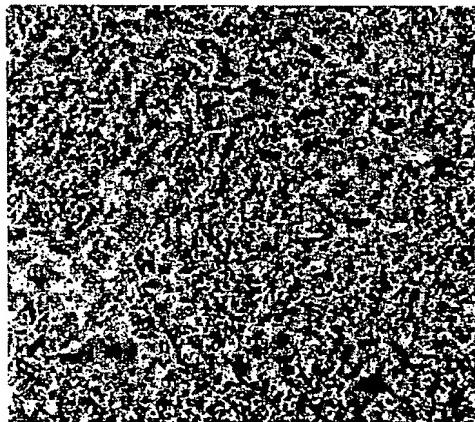


Figure 2B

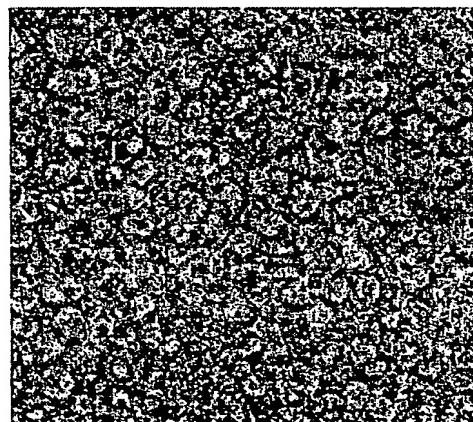


Figure 3 (gel according to Example V)



Figure 4 (gel according to Example VI)

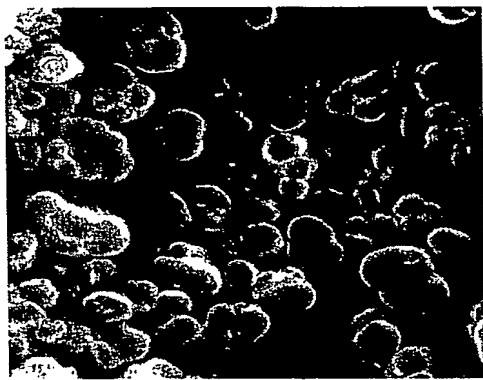
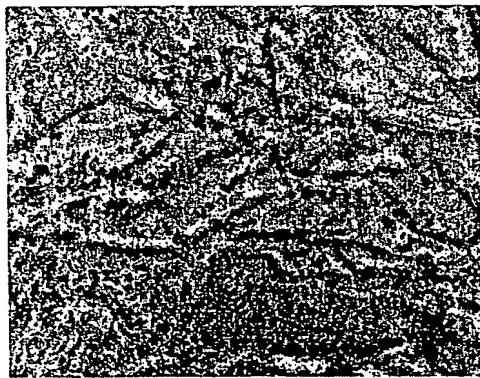


Figure 5 (gel according to Example VII)



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INTERNATIONAL SEARCH REPORT

Patent Application No
PCT/NL2004/000093

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08B30/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 188 674 A (KASICA JAMES J ET AL) 23 February 1993 (1993-02-23) cited in the application claims 1,7,8 ---	1,2,11, 14-24
X	US 3 951 947 A (SCHANEFELT ROBERT V ET AL) 20 April 1976 (1976-04-20) claims 1,2; example I column 2, line 11 - line 20 column 3, line 51 - line 58 ---	20-27 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

Date of mailing of the international search report

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17/05/2004

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Schütte, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL2004/000093

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 547 513 A (STONE JOEL A ET AL) 20 August 1996 (1996-08-20) column 4, line 2 - line 3 column 5, line 20 - line 24 column 5, line 65 -column 6, line 9 column 6, line 65 -column 7, line 6 column 8, line 11 - line 16 column 8, line 48 - line 52 -----	1,20

INTERNATIONAL SEARCH REPORT

Regional Application No

PCT/NL2004/000093

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 5188674	A	23-02-1993	US	5131953 A		21-07-1992
			US	5435851 A		25-07-1995
			US	5571552 A		05-11-1996
			US	5318635 A		07-06-1994
			AU	609331 B2		26-04-1991
			AU	4111789 A		15-03-1990
			DE	68925612 D1		21-03-1996
			DE	68925612 T2		13-06-1996
			EP	0366898 A1		09-05-1990
			JP	2150401 A		08-06-1990
			JP	2511534 B2		26-06-1996
US 3951947	A	20-04-1976	AU	503143 B2		23-08-1979
			AU	8493075 A		21-04-1977
			BE	833491 A4		17-03-1976
			CA	1014553 A1		26-07-1977
			DE	2541513 A1		25-03-1976
			FR	2285401 A2		16-04-1976
			GB	1517395 A		12-07-1978
			IT	1047707 B		20-10-1980
			JP	51076375 A		01-07-1976
			NL	7510906 A		19-03-1976
			NZ	178696 A		28-07-1978
			AU	7190474 A		05-02-1976
			BE	818492 A4		05-02-1975
			DE	2435960 A1		20-02-1975
			FR	2240235 A2		07-03-1975
			GB	1447908 A		02-09-1976
			IT	1056066 B		30-01-1982
			JP	50049382 A		02-05-1975
			NL	7410756 A		12-02-1975
US 5547513	A	20-08-1996	US	5470391 A		28-11-1995
			AT	195633 T		15-09-2000
			AU	8017094 A		04-05-1995
			DE	69425663 D1		28-09-2000
			DE	69425663 T2		07-06-2001
			EP	0723403 A1		31-07-1996
			US	5584937 A		17-12-1996
			CA	2174211 A1		20-04-1995
			WO	9510196 A1		20-04-1995
			US	5679395 A		21-10-1997
			US	5679396 A		21-10-1997